

## ACTIVITY AND CHARACTERIZATION OF COPROCESSING CATALYSTS PRODUCED FROM AN IRON PENTACARBONYL PRECURSOR

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### ABSTRACT

It is generally believed that highly dispersed catalysts are very effective in the conversion of coal to liquids, but the effects of dispersion and composition have not been adequately investigated. We chose to study the use of iron pentacarbonyl,  $\text{Fe}(\text{CO})_5$ , to produce a highly dispersed catalyst *in situ* in the coprocessing of Illinois #6 coal and Maya ATB residuum. The activity of the catalyst produced from this precursor has been investigated, and its particle size and composition measured using X-ray diffraction, Mössbauer spectroscopy, and transmission electron microscopy (TEM). Use of 0.5 wt% Fe added as  $\text{Fe}(\text{CO})_5$  resulted in an increase in coal conversion to methylene chloride solubles from 39% to 82%. The  $\text{Fe}(\text{CO})_5$  precursor decomposed in the reactor to produce a mixture of highly dispersed pyrrhotite,  $(\text{Fe}_{1-x}\text{S})$ ,  $\text{Fe}_3\text{C}$ , and other iron compounds. However, with time at reaction conditions, 95% of the iron was converted to  $\text{Fe}_{1-x}\text{S}$ . The pyrrhotite particles formed in the initial stages of reaction had a mean crystallite size of 12 nm when measured using X-ray diffraction line broadening; the small particle sizes were confirmed by TEM and Mössbauer studies.

### INTRODUCTION

Coprocessing is the liquefaction of coal in a heavy petroleum medium such as a heavy crude or residuum. Conventional direct liquefaction processes must recycle two-thirds of the coal-derived oil, but coprocessing can operate completely or largely in a "once through" mode, eliminating the cost and complication of the large recycle. (1) In addition, metallic impurities in the oil deposit on the coal residue or pitch.

In most direct coal liquefaction processes, the use of catalysts results in more desirable products under less severe processing conditions. The same is true for coprocessing, which may require even more effective catalysts because the petroleum-derived slurrying oils used in coprocessing are often poor hydrogen donors. In direct coal liquefaction, supported metal catalysts (e.g.  $\text{CoMo}/\text{Al}_2\text{O}_3$ ) may suffer from poor contact between the coal and the catalyst. Unsupported dispersed catalysts can offer good contact between the coal and the catalyst. As early as 1924 it was known that the addition of iron sulfides to the liquefaction mixture would improve yields. (2) Addition of low surface area solids requires high catalyst concentrations. Particulate pyrite addition has been studied and found effective in concentrations of 10wt%. (3)

One method of increasing dispersion (surface area per mass) is to introduce the catalyst as a soluble precursor. Such precursors are distributed throughout the coal-oil mixture by

dissolving in the oil, and they decompose upon heating or other treatment to form very small catalyst particles within the coal-oil mixture. The high dispersion allows catalyst concentrations of less than 1.0wt% to be used. Examples of these catalyst precursors are nickel acetate, (4) carboxylic salts of iron or molybdenum, (5) water-soluble ammonium molybdate, (6) molybdenum naphthenate (7), and carbonyl compounds of iron, molybdenum, and other metals. (8) Crystallite sizes as low as 15-30nm have been reported for a Ni acetate precursor. (4)

Several studies have reported the use of  $\text{Fe}(\text{CO})_5$  and other iron carbonyls in direct liquefaction in a hydrogen-donating solvent. (9-12) These studies showed that the  $\text{Fe}(\text{CO})_5$  precursor produced a catalyst active for hydrol liquefaction of coal using Fe at 2.0wt% of the feed coal. The precursor was converted to a less active iron oxide ( $\text{Fe}_3\text{O}_4$ ) in the absence of added sulfur, but when sulfur was added in the form of elemental sulfur or organic sulfur compounds, the more active iron pyrrhotite ( $\text{Fe}_{1-x}\text{S}$ ) was formed. (10) Increases in coal conversion were found with both bituminous and subbituminous coals. (11) The use of other soluble precursors such as cyclopentadienyliron dicarbonyl dimer,  $(\text{C}_5\text{H}_5)_2\text{Fe}_2(\text{CO})_4$ , yielded increased coal conversions of the same order of magnitude as  $\text{Fe}(\text{CO})_5$ . (8) However, particle sizes of liquefaction catalysts produced from the decomposition of  $\text{Fe}(\text{CO})_5$  have not been reported in the literature, but other studies have shown that iron particles less than 10nm in diameter can be deposited on carbon or zeolite supports by thermal decomposition. (12,13)

## EXPERIMENTAL

Illinois #6 (Burning Star) hvB bituminous coal ground to -200 mesh ( $<74\mu\text{m}$ ) was obtained from the Pittsburgh Energy Technology Center and used as received. Maya ATB (650°F+) residuum was obtained from Citgo. Analysis of the coal is shown in Table 1. The Maya ATB had a composition of 85.9%C, 10.2%H, 0.5%N, and 4.8%S, with a Conradson Carbon residue of 15.2%. Iron pentacarbonyl was obtained from Strem Chemical and filtered through glass wool when necessary to remove iron particles produced by decomposition of the carbonyl.

**Table 1.** Ultimate and Proximate Analyses of Illinois #6 Coal

	wt. %		wt. %
Carbon	74.0	Organic Sulfur	0.96
Hydrogen	5.65	Moisture	3.80
Nitrogen	1.58	Volatile Matter	40.5
Sulfur	3.07	Fixed Carbon (diff.)	48.7
Ash	10.8		
Oxygen (diff.)	4.90		

Ultimate analysis is on a dry basis

Analyses performed by BCR National Laboratory

Coprocessing experiments were conducted in a 300ml stainless steel autoclave (Autoclave Engineers) agitated by a turbine impeller and heated by a tube furnace. Coal (12.5g, as rec.), 37.5g Maya ATB residuum, and from 0-8.8g (0-5wt%Fe) catalyst precursor were placed into the reactor, which was flushed with helium and stirred at 50°C for two hours

to ensure mixing of the precursor in the viscous residuum. The reactor was pressurized with hydrogen to 6.9 MPa, heated to 425°C in approximately 40 minutes, and held at 425°C for 60 minutes while stirring at 1300 rpm. The reactor was then cooled to below 300°C in about five minutes. Conversion was determined using Soxhlet extraction with methylene chloride. Soluble products were recovered by rotary evaporation at 45°C under vacuum. Pentane solubles were determined by adding 40 volumes of n-pentane to the methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) solubles, and using Soxhlet extraction with pentane.

A Phillips X-ray Diffractometer using  $\text{Cu-K}\alpha$  radiation at 30kV and 20mA was used to obtain powder diffraction patterns of the catalysts. The Scherrer equation was used to calculate average crystallite sizes from line broadening of the peaks, corrected for instrumental broadening. (14) Mössbauer spectroscopy was performed using a 100 mCi source at both room temperature (290K) and cryogenic temperatures (10K, 80K). Transmission electron microscopy was carried out using a JEOL 2000FX STEM (100kV beam) with an energy dispersive X-ray spectrometer. A Bruker MSL 300 FT-nuclear magnetic resonance spectrometer was used to obtain the carbon aromaticity ( $f_a$ ) of soluble coprocessing products.

## RESULTS AND DISCUSSION

Coprocessing of Illinois #6 coal with Maya ATB was carried out with varying amounts of  $\text{Fe}(\text{CO})_5$  precursor. The conversion to methylene chloride solubles increased rapidly as the catalyst concentration was raised from 0 to 0.5 wt% Fe (based on the total coal + residuum feed), but increased much more slowly from 0.5 to 5wt% Fe (Figure 1). The use of only 0.2 wt% Fe was sufficient to increase conversion to 65%, vs. 39% for the no-catalyst case. The fact that an amount of iron considerably less than that already present in the coal can produce such an increase shows the benefit of using a precursor which will give high dispersion.

The effect of the iron catalyst produced from the precursor appears to be limited to conversion of the coal rather than hydrogenation of the residuum or subsequent upgrading of the coal liquids produced. Catalyst addition produced little change in the asphaltene fraction of the product (it increased from 12% of the product to 15%). Table 2 shows that the H/C ratio of the products does not change significantly with catalyst addition, and heteroatoms are not removed to any appreciable extent. The aromaticity ( $f_a$ ) of the  $\text{CH}_2\text{Cl}_2$  solubles does increase with catalyst addition due to the high aromaticity of the additional liquids produced from the coal.

**Table 2.** Analyses of  $\text{CH}_2\text{Cl}_2$  Solubles from Coprocessing using a  $\text{Fe}(\text{CO})_5$  Catalyst Precursor

$\text{Fe}(\text{CO})_5$ (wt% Fe)	wt.%, as received					$f_a$
	C	H	N	S	H/C(atom)	
0.0	83.3	10.5	0.2	2.6	1.49	0.36*
2.5	83.1	10.6	n.d.	2.6	1.53	0.40
5.0	84.0	10.6	0.3	2.4	1.51	---

\* $f_a$  of Maya ATB is 0.33

XRD and Mössbauer spectroscopy were used to determine the composition and

dispersion of the catalysts produced from  $\text{Fe}(\text{CO})_5$ . The results are presented in Table 3. The properties of the catalyst at various stages of reaction were of interest, so a number of samples of insoluble coprocessing residue were analyzed. The first sample (referred to as 425°C - 0 min.) was prepared by heating a mixture of coal, residuum, and  $\text{Fe}(\text{CO})_5$  (2.5 wt% Fe) to the reaction temperature of 425°C, then cooling the mixture immediately. This sample represents the condition of the catalyst before extensive coal conversion has taken place. X-ray diffraction patterns of this sample showed a fully developed pyrrhotite pattern. This result agrees with the results of Suzuki et al. (10), and should be expected since the Maya residuum is high in sulfur (4.84 wt%). A line broadening calculation on the largest pyrrhotite peak gave an average crystallite diameter of 12.0nm.

The second sample (425°C - 60 min.) consisted of the insoluble residue which remained after reaction of coal, residuum, and  $\text{Fe}(\text{CO})_5$  for 60 minutes at 425°C. This sample represented the state of the catalyst after it had spent a longer time under the reaction conditions. This sample also showed a pyrrhotite pattern, but with an average crystallite diameter of 20.5nm. The increase in crystallite size is likely due to the sintering of small metal catalyst particles which commonly occurs at elevated temperatures. (15) Djega-Mariadassou et al. found that when iron oxide aerosols (<80nm) were used as liquefaction catalysts, the small particles were very sensitive to sintering, but in the presence of coal the effect was inhibited. (16) This was attributed to the coal depositing heavy organic residues on the surface of the catalyst.

In order to distinguish the iron added as  $\text{Fe}(\text{CO})_5$  from the iron originally present in the coal, XRD and Mössbauer spectroscopy were performed on a sample of Illinois #6 coal and on a coprocessing residue to which no catalyst had been added. Table 3 shows that the coal exhibited only a weak diffraction pattern for  $\text{FeS}_2$ , and that the coprocessing sample without added  $\text{Fe}(\text{CO})_5$  gave a weak  $\text{Fe}_{1-x}\text{S}$  pattern. Since these patterns were weak compared to the samples with added catalyst, it was concluded that the XRD signal was mostly due to the added catalyst.

Mössbauer spectroscopy confirmed the presence of the pyrrhotite detected by XRD, but revealed some other species which were, perhaps because of their small particle size or lack of crystallinity, invisible to XRD. The 425°C - 0min. sample was found to consist of only 26% pyrrhotite, with about an equal amount of iron carbide and almost 50% of iron oxide/oxyhydroxide. The oxide/oxyhydroxide may have been produced in the reaction, or it may have been originally  $\alpha\text{-Fe}$  which was oxidized when the sample was exposed to air. In any case, it is interesting to see that the precursor may form a variety of iron compounds in the reactor. The source of the iron carbide is probably  $\text{Fe}(\text{CO})_5$  and not the pyrite originally in the coal, since the transformation of pyrite to iron carbide is thermodynamically unfavorable under these conditions. Cook and Cashion have also observed the formation of iron carbide from  $\text{Fe}_3(\text{CO})_{12}$  when they used it as a catalyst precursor in the liquefaction of a brown coal. (17) Mössbauer analysis of the 425°C - 60 min. sample showed that after 60 minutes at the reaction conditions, most of these intermediates had been transformed to pyrrhotite, with a small amount of iron oxide remaining. In the high-sulfur environment of the coprocessing reaction, it is thermodynamically favorable for all of the iron to be converted to pyrrhotite.

The Mössbauer results show that the pyrrhotite was not the common mineralogical type, monoclinic  $\text{Fe}_7\text{S}_8$ , but was a somewhat poorly formed intermediate variety. In addition to the composition, the Mössbauer spectra provided information as to the size of the catalyst particles. There was a significant difference between the room temperature spectrum and those obtained at cryogenic temperatures, indicating the presence of superparamagnetic iron-bearing particles, which only occurs when particles are on the order of 20nm or less. (18)

Transmission electron microscopy was employed to independently verify the size range of the iron-containing particles produced from the  $\text{Fe}(\text{CO})_5$  precursor. To eliminate interference of the iron and other mineral matter in the coal, a model catalyst system was used which consisted of activated carbon with iron deposited on it. The model catalyst was produced by heating a mixture of activated carbon (with a very low iron content), toluene

**Table 3.** X-ray Diffraction and  $^{57}\text{Fe}$ -Mössbauer Data for Products of  $\text{Fe}(\text{CO})_5$  Decomposition

<u>Sample</u>	<u><math>^{57}\text{Fe}</math> Mössbauer Phases (%iron)</u>	<u>XRD - Iron Phases Identified (mean diam.)</u>
Coprocessing Residue 425°C, 0 min. $\text{Fe}(\text{CO})_5$ precursor	$\text{Fe}_{1-x}\text{S}$ (26%) $\text{Fe}_3\text{C}$ (25%) Iron oxide/ $\text{FeOOH}$ (49%)	$\text{Fe}_{1-x}\text{S}$ (12.0nm)
Coprocessing Residue 425°C, 60 min. $\text{Fe}(\text{CO})_5$ precursor	$\text{Fe}_{1-x}\text{S}$ (95%) Iron oxide (5%)	$\text{Fe}_{1-x}\text{S}$ (20.5nm)
Coprocessing Residue 425°C, 1hr. No catalyst added	$\text{Fe}_{1-x}\text{S}$ (~100%) Iron oxide (trace)	$\text{Fe}_{1-x}\text{S}$ - trace
Illinois #6 coal - Before Reaction	Pyrite (87%) $\text{FeSO}_4 \cdot \text{H}_2\text{O}$ (8%) Ferric sulfate (5%) $\text{FeOOH}$ (trace)	$\text{FeS}_2$ - trace

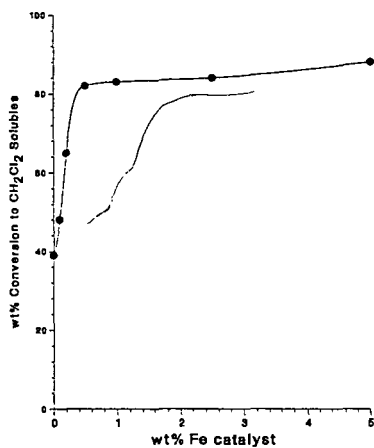
(solvent), and  $\text{Fe}(\text{CO})_5$  in an autoclave to decompose the precursor into small particles, some of which would end up on the carbon support. The TEM/STEM images of this catalyst system revealed a wide distribution of particle sizes, with many particles between 10-100nm. Energy dispersive analysis of the X-rays emitted from the sample confirmed that the small particles which were observed contained iron, while the matrix as well as the activated carbon blank contained no detectable iron. A typical micrograph is shown in Figure 2, exhibiting the iron-bearing particles (small, dark spots) on the more transparent background of the larger activated carbon particle.

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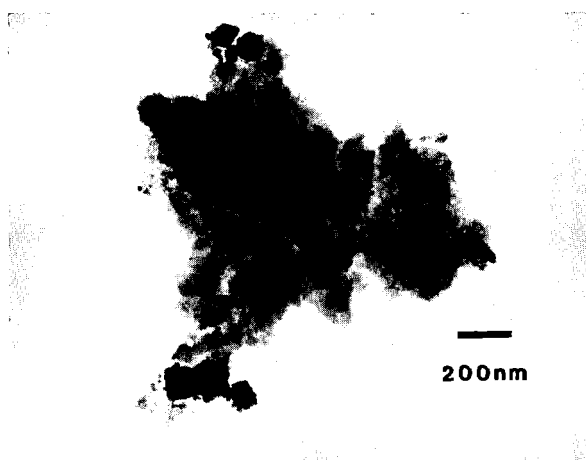
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**Figure 1.** Coal Conversion vs. Amount of  $\text{Fe}(\text{CO})_5$  Precursor



**Figure 2.** TEM/STEM Micrograph of Iron-Containing Particles Deposited on Activated Carbon by Thermal Decomposition of  $\text{Fe}(\text{CO})_5$